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Opacifying Agents for Glazes, with Especial Reference to Alumina as an Opacifier

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OPACIFYING AGENTS FOR GLAZES: WITH ESPECIAL REFERENCE TO ALUMINA AS AN OPACIFIER

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Elmer Holmes Van Schoick

ENTITLED Opacifying Agents for Glazes With Especial Reference to Alumina as an Opacifier.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Ceramic Engineering

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INTRODUCTION

Langenbeck[1] defines an enamel as "a nontransparent glass, completely covering the body on which it is melted, the nontransparency being due to the presence of tin oxide, arsenic, bone-ash or cryolite".

Seger[2] gives as opacifiers "tin oxide antimonic acid, arsenic acid and large quantities of alumina".

To these lists may be added zinc oxide,[3] the opacifying properties of which are well known, magnesium oxide,[4] and boric oxide when it functions as a base.[5]

Some of the opacifiers, notably zinc, magnesia and alumina, when present in small amounts will dissolve in the fused mixture and the resulting glaze will be clear. If present in larger amounts, they may or may not be taken into solution when the glaze is fused, and if in solution they will be precipitated or crystallized out or may remain in suspension when the glaze has cooled. In either case the resulting glaze will be more or less opaque.

In order to develop an opaque glaze which will be desirable for stone ware and other cheap, bulky products, the use

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1. Chemistry of Pottery, p. 45.
2. Collected writings Vol. II, p. 559.
3. Purdy "Stone ware Glazes". Transactions American Ceramic Society, Vol. IV. p. 69.
4. Stull "A Cheap Enamel for Stone ware" Transactions American Ceramic Society, Vol. XI, p. 605.
5. Ibid Stull "Opalesence and Function of B_2O_3 in the Glaze". Transactions American Ceramic Society, Vol. XVI, p. 130.

of expensive ingredients such as tin oxide must be avoided as far as possible. Alumina, whether added as feldspar, cornwall stone or clay, is one of the cheapest ingredients of the glaze, and if a good opaque glaze can be made with alumina as the opacifier the cost of the glaze will be considerably less than if the more expensive oxides are resorted to. The practical glaze makers do not seem to have realized the value of the high alumina glazes for enamelling purposes.[1]

Although several writers have suggested the use of Al_2O_3 for obtaining opacity, they do not distinguish between the effects of the different minerals, in which the Al_2O_3 may be added, upon the resulting glaze. It has been shown that it is impossible to reproduce an Albany slip glaze by making up a mixture according to the chemical analysis of the raw slip.[2] The mineral form of the ingredients seemed to be an important factor as well as the chemical amount. Similarly we might expect to get different results from a certain amount of Al_2O_3 added as clay and an equivalent amount added as feldspar or Cornwall stone. Thus the problem is not only to determine the amount of Al_2O_3 which can permissibly be used in the glaze formula, but to determine also the best mineral source for this alumina.

The object of this investigation was to develop cheap enamels for clay-ware at temperatures ranging from cone 3 to cone 9 without the use of tin oxide or other expensive opacifying agents.

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1. Purdy "Bristol Glazes" Transactions American Ceramic Society, Vol. V, p. 137.
2. Orton. Transactions American Ceramic Society, Vol. IV, p. 77.

For the higher temperatures a glaze of the Bristol or stoneware type was to be developed, and then this glaze was to be softened down so as to mature at cone 2 or 3.

Although no definite outline for the work was adopted, the investigation falls naturally into two divisions,

(1) The development of enamels at cone 8 or 9.

(2) The development of enamels at cone 2 or 3.

The method of investigation which developed after the work was under way, was to take the best glaze of each series and attempt to improve its desirable qualities in another series of which it was the base.

MATERIALS USED.

Clay for trial pieces: -- The clay used for test pieces was the so-called Bloomingdale Stoneware clay from Bloomingdale, Indiana. This is a Number 2 fire clay having good plasticity, low shrinkage and good working qualities. It burns to a dense, bluish-gray body at cone 8 and to a porous, light-buff body at cone 3.

GLAZE MATERIALS.

Feldspar: -- "Brandywine Summit" potash feldspar.

Clays: -- 1. Tennessee Ball Clay No. 7.

2. "M.G.R." English China Clay.

Flint: -- Ohio eight-hour grind.

Whiting, zinc oxide and white lead: -- the ordinary commercial material.

Magnesia: -- Magnesite rock washed, crushed and ground to 80 mesh was the source of the magnesia.

METHOD OF PREPARING GLAZES.

The field to be investigated was determined on, and a rectangular or triaxial diagram was plotted to include the variations desired. The batch weights of the corner glazes were calculated from their formulae and a sufficient quantity of each was made up to allow the intermediate glazes to be blended from them. The molecular weights of these corner glazes determined the proportions by which they were blended in the intermediate glazes, so that the formula of any glaze might be read directly from the diagram of the field.

The glaze materials were weighed up dry, wet ground for

about two hours in a porcelain lined ball mill, and screened through a 120 mesh sieve. The glaze was then allowed to stand until the excess water could be decanted. After decantation the glazes were set at 1600 degrees on the scale of the B. and L. hydrometer and the moisture factor determined. They were then blended according to the calculated tables, so that the variations between variable components of glazes in the same series were by molecules or fractions thereof.

TRIAL PIECES.

Bloomingdale stone ware clay was screened, pugged in a wet-pan, and run through a small auger machine. The column was 4 1/2 inches wide and 5/8 inches thick, and was cut into trial pieces 2 inches wide and 2 1/4 inches long. The trials were dried in an open room.

DIPPING.

All glazes were dipped on bone-dry trial pieces. The coating applied was somewhat thicker than that given to the average stoneware. An attempt was made to dip all glazes to a uniform thickness. At least two trials of each glaze were dipped.

The pieces were usually allowed to stand over night before setting in the kiln.

BURNING.

The trials were set flat in tile saggers and burned in the down-draft, open-fire kiln of the Ceramic laboratory at the University.

Cones were placed in each sagger so as to overcome any

error in conclusions due to variations in temperature in the kiln chamber. Different trials of the same glaze were placed in separate saggers so as to determine the temperature range of the glaze in so far as this could be done at one burn.

The kiln was fired with coke; the average time of burning was about 24 hours.

SERIES I.

The first series was simply a porcelain glaze field, the R.O. being of the regular porcelain type, i.e. $\left.\begin{matrix} .35\ K_2O \\ .65\ CaO \end{matrix}\right)$ with variable silica and alumina, outlined on a rectangular diagram.

Series I included 36 glazes and covered the following field:

$$\left.\begin{matrix} .35\ K_2O \\ .65\ CaO \end{matrix}\right)\ .35 \text{ to } .75\ Al_2O_3 \quad 2.1 \text{ to } 5.6\ SiO_2$$

The limits were set wide enough to cover almost the entire field of good glazes.

The four corner glazes from which the rest were blended were as follows:

A - 1 Low Al_2O_3 and Low SiO_2

$$\left.\begin{matrix} .35\ K_2O \\ .65\ CaO \end{matrix}\right)\ .35\ Al_2O_3 \quad 2.1\ SiO2$$

A - 6 Low Al_2O_3 and High SiO_2

$$\left.\begin{matrix} .35\ K_2O \\ .65\ CaO \end{matrix}\right)\ .35\ Al_2O_3 \quad 5.6\ SiO_2$$

F - 1 High Al_2O_3 and Low SiO_2

$$\left.\begin{array}{l} .35\ K_2O \\ .65\ CaO \end{array}\right) \quad .75\ Al_2O_3 \quad 2.1\ SiO2$$

F - 6 High Al_2O_3 and High SiO_2

$$\left.\begin{array}{l} .35\ K_2O \\ .65\ CaO \end{array}\right) \quad .75\ Al_2O_3 \quad 5.6\ SiO_2$$

The silica content increased horizontally from left to right, the variation being .7 molecules for each glaze. The alumina content varied from top to bottom of the field, the variation being .08 molecules for each glaze.

These glazes were prepared, blended and dipped as described. They were burned to cone 8 and 9 in 24 hours.

RESULTS OF SERIES I.

By an inspection of the diagram of series I, it will be seen that almost the entire field of good glazes of this especial type was covered.

In series A crazing was encountered in the low silica glazes, and this has been overcome by increasing the silica content, so that A - 4, A - 5 and A - 6 are not crazed. This conforms with Seger's rule for overcoming crazing by increasing the SiO_2 in the glaze.[1] A - 6 does not produce a bright glaze at cone 8. A - 5 and A - 6 showed a slight opacity due to devitrification.

The B series showed the same general characteristics except that B - 1 is not matured.

The first evidences of opacity due to alumina were

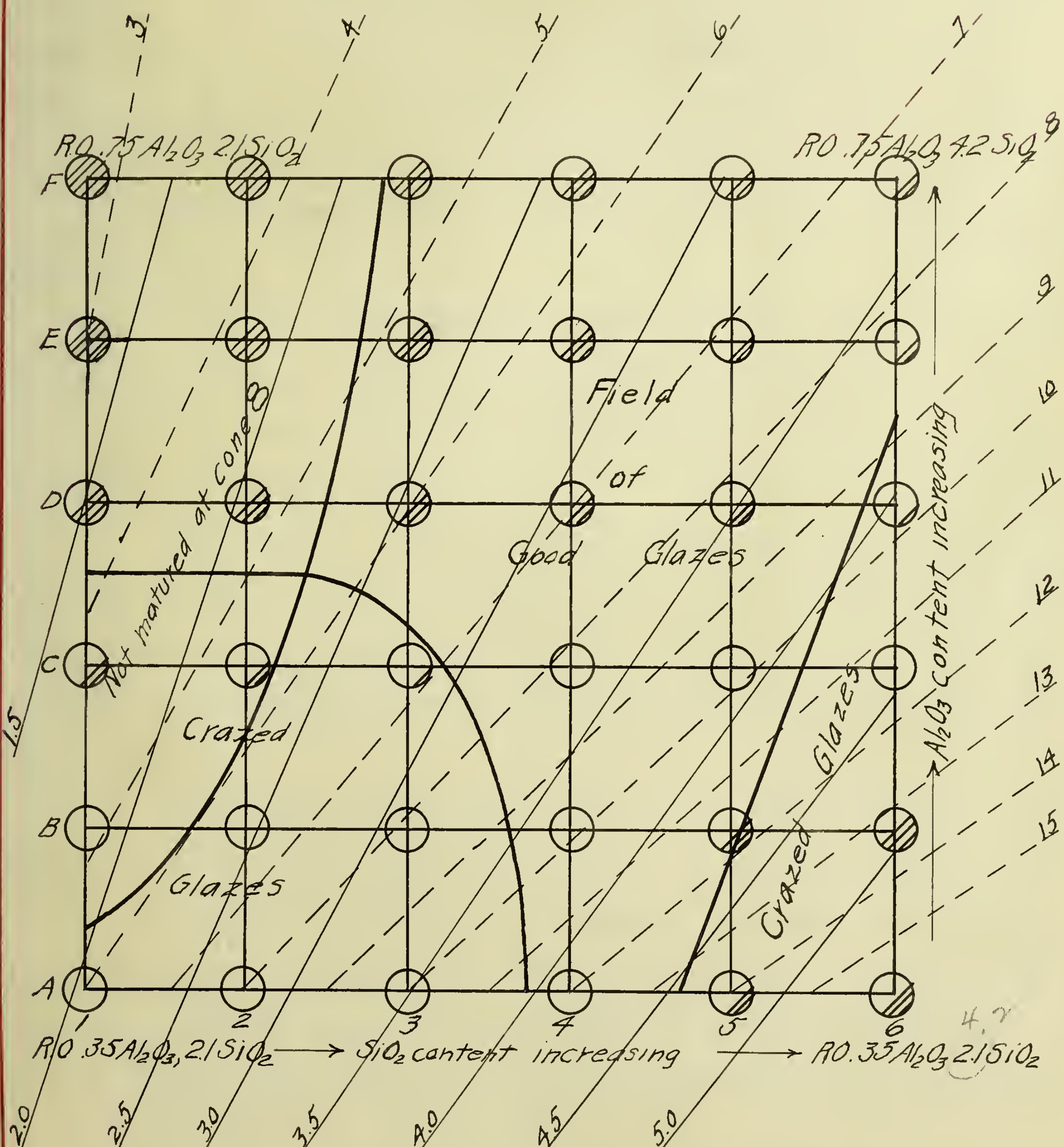
1.Seger "Collected Writings Vol. II, p. 581.
Langenbeck "Chemistry of Pottery" p. 50

FIGURE I

SERIES-I

$\left.\begin{matrix}.35K_2O\\.65CaO\end{matrix}\right\}$ .35 to .75 Al_2O_3 2.1 to 4.2 SiO_2

Burned to cone 8



Lines of equal total oxygen ratio.

Lines of equal molecular ratio Al_2O_3 to SiO_2

Shading of circles indicates degree of opacity.

observed in the C series. Crazing is encountered in both the high and low silica glazes of this series.

In the D series the whiteness due to Al_2O_3 is still more noticable. No crazing was present except in the highest silica glaze D - 6. D - 1 and D - 2 are not ~~are not~~ matured. In this series the decrease in whiteness and opacity from left to right, i.e. with increase in silica, is clearly shown.

The E series is as a whole whiter than D. No clear glazes can be found.

F series - This series showed a further increase in whiteness and opacity, F 4 was the most opaque glaze in this series. F - 5 and F - 6 were better developed than F - 4, which was rather dull, but showed less opacity.

From Figure I it will be seen that the glazes which showed the best opacity together with brilliancy and good fitting qualities were those having a total oxygen ratio of between 1 to 2.5 and 1 to 3, and a molecular ratio of alumina to silica of from 1 to 5 up to 1 to 6.

The best opaque glazes were D - 3 (R.O .59 Al_2O_3 .35 SiO_2) E - 4 (R.O. .67 Al_2O_3 4.2 SiO_2) and F - 4 (R.O. .75 Al_2O_3 4.2 SiO_2)

It may be noted that no flaking, crawling, bubbling or pinholing were observed. The only defects being crazing in low alumina-low silica glazes, devitrification in low alumina-high silica glazes, and immaturity in high alumina-low silica glazes.

CONCLUSIONS FROM SERIES I.

1. Both high alumina and high silica will produce a fair degree of opacity, which in the case of the high silica is probably

due to devitrification. High silica glazes are liable to craze, but fairly opaque glazes may be obtained with high alumina which will fit the body perfectly.

2. An equivalent of Al_2O_3 at least as high as .75 may be used without bad effect, but the SiO_2 must also be at least as high as 4.2.

3. An Oxygen ratio of 2.5 to 3 is best at this temperature (cone 8)

4. A molecular ratio of Al_2O_3 to SiO_2 of 1 to 5 up to 1 to 6 is best at cone 8.

SERIES II, III AND IV.

The object of these three similar series was to develop the opacity of the best glazes in series I, by the use of magnesia and zinc oxide.

In each case part of the CaO in the original glaze was replaced by MgO and ZnO. The limits covered were

.65 to 0	CaO
0 to .65	ZnO
0 to .65	MgO

Each series consisted of 21 glazes forming a triaxial field with six glazes to the side.

SERIES II.

Glaze F - 4 of Series I was the base of Series II. Its formula was $\left.\begin{matrix} .35\ K_2O \\ .65\ CaO \end{matrix}\right)$ $.75\ Al_2O_3$ $4.2\ SiO_2$. In Series II this became glaze 21, one of the corner glazes.

Glaze 1 was $\left.\begin{array}{l}.35\ K_2O \\ .65\ MgO\end{array}\right)$ $.75\ Al_2O_3$ $4.2\ SiO_2$. Glaze 6 was $\left.\begin{array}{l}.35\ K_2O \\ .65\ ZnO\end{array}\right)$ $.75\ Al_2O_3$ $4.2\ SiO_2$.

By blending these glazes so as to make four intermediate glazes between corners a variation of .13 equivalents of MgO, ZnO and CaO was obtained throughout the field.

Series II, III and IV were burned at the same time to cone 8 in 23 hours.

RESULTS OF SERIES II.

The most opaque and whitest glazes were obtained in the lower right hand corner of the field, these were the highest in ZnO (see Figure II). But in the same section occurred the poorest fitting glazes, and although the glazes were very white, they lacked the life and luster of those higher in lime and magnesia.

The opacifying effect of magnesia was seen by observing the increase in opacity along the line of zero zinc oxide between glazes 1 and 21. But this high content of magnesia made a too refractory mixture, and immatured glazes were found in the lower left hand corner.

The best glazes, considering gloss, whiteness and opacity, occurred slightly below the middle of the field. Glazes 8, 9, 10, 13 and 14 were the best in the series, and of these glaze 14 was the one selected as the best.

The formula of glaze 14 is

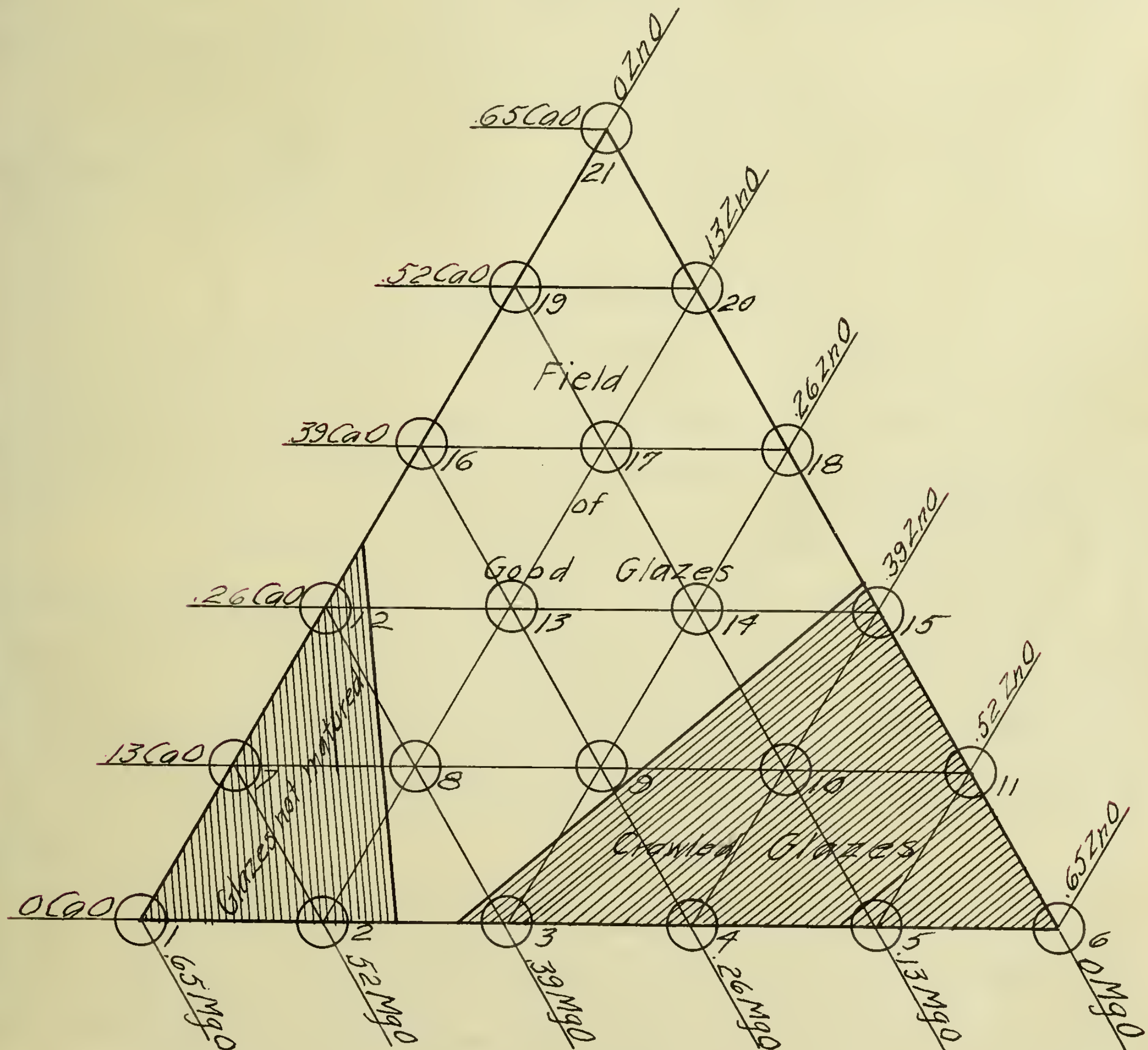
$$\left.\begin{array}{l}.35\ K_2O \\ .26\ CaO \\ .26\ ZnO \\ .13\ MgO\end{array}\right)\ .75\ Al_2O_3\quad 4.2\ SiO_2$$

FIGURE II

SERIES II

$$\left.\begin{array}{l} .35\,K_2O \\ 0-.65\,CaO \\ 0-.65\,ZnO \\ 0-.65\,MgO \end{array}\right\}\ .75\,Al_2O_3\ \ 4.2\,SiO_2$$

Burned to cone 8



This glaze is much whiter and has a better gloss than the average commercial stone ware glaze.

SERIES III.

Series III was similar to Series II in the variations made and field covered. The difference was a lower alumina content with the same silica content.

The base of this Series was glaze E - 4, Series I, of the formula $\left.\begin{array}{l} .35\ K_2O \\ .65\ CaO \end{array}\right)$ $.67\ Al_2O_3$ $4.2\ SiO_2$.

RESULTS OF SERIES III.

The same general results due to increasing magnesia and zinc in Series II were observed in Series III. Corresponding glazes of the two series differed in two respects very noticeably.

1. The opacity and whiteness of glazes in Series II is greater than in those of corresponding R.O. in Series III. Since the glazes of the two series were set at the same density and an effort was made to keep the coating uniform, there is no ground for believing that this difference was due to anything but the higher alumina content in Series II.

2. Crawling, due to high ZnO, was more pronounced in Series III than on corresponding trials of Series II. This was attributed to the lower molecular weight of the Series III glazes. The capacity for dissolving the ZnO and forming a perfect fitting glaze is evidently decreased.

SERIES IV.

Series IV was the third of the three series used to

develop the best glazes of Series I. The silica and alumina content of this series were both lower than those of Series III. The field covered and the variations made were the same as in II and III. The base of this series was glaze D - 3 of Series I.

$$\left.\begin{array}{l} .35\ K_2O \\ .65\ CaO \end{array}\right)\ .59\ Al_2O_3\ \ 3.5\ SiO_2$$

RESULTS OF SERIES IV.

The trial pieces showed the same general appearance as those in Series II and III, the effect of the ZnO and MgO being observed as before. The series as a whole showed a decrease in whiteness and opacity from Series III. It was again noticed as in Series III that the crawling was more pronounced with the lower Al_2O_3 glazes.

GENERAL CONCLUSIONS FROM SERIES II, III AND IV.

1. Both MgO and ZnO exert an opacifying influence on the glaze mixture, but neither gives as good results when used alone as when both are included in the R.O., which agrees with Stull's results[2].

2. When more than .26 CaO was replaced by MgO, the glazes were not matured at cone 8.

When more than .26 CaO was replaced by ZnO crawling resulted.

When both ZnO and MgO were used in the R.O, as high as

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1. Stull "A Cheap Enamel for Stoneware" Transactions American Ceramic Society. Vol. IX, p. 605.

.52 CaO could be replaced without causing defects in the glaze.

3. With a glaze containing .75 Al_2O_3 and 4.2 SiO_2 the best relation between the oxides was found to be

.35 K_2O
.13 MgO
.26 ZnO
.26 CaO

4. As the alumina and silica was decreased in the glazes, the same amount of ZnO had a more pronounced effect in causing crawling.

5. The gloss and whiteness of the good glazes was much better in those containing higher alumina content.

SERIES V AND VI.

In order to test the effect of a substitution of clay for spar in a good Bristol glaze, a triaxial diagram was constructed varying K_2O, ZnO and MgO. Since alumina and silica are constant and the feldspar content must vary, the clay content must also vary. Thus those glazes having low K_2O content will have a high clay content and vica versa.

The limits of the series were selected so as to include the best glazes in Series II and III. K_2O was varied from .3 to .5, MgO from .1 to .3, and ZnO .15 to .35. The CaO content was constant at .25.

Each series consists of 15 glazes burned to cone 8.

SERIES V. -- Alumina-Silica content corresponding to that of Series II.

Three corner glazes were made up and intermediate glazes blended from them.

Glaze 1.	.3 K_2O .25 CaO .30 MgO .15 ZnO	.75 Al_2O_3	4.2 SiO_2
Glaze 5.	.3 K_2O .25 CaO .1 MgO .35 ZnO	.75 Al_2O_3	4.2 SiO_2
Glaze 15	.5 K_2O .25 CaO .1 MgO .15 ZnO	.75 Al_2O_3	4.2 SiO_2

By blending three glazes between each two corner glazes a variation of .05 K_2O, .05 ZnO and .05 MgO was obtained throughout the field.

Series V was burned with Series VI to cone 8 in 25 hours.

SERIES VI.

The variation of R.O and the field covered was the same as in Series V. The only difference was in the alumina content, which corresponded to that used in Series III, viz: R.O., 67 Al_2O_3 4.2 SiO_2.

RESULTS OF SERIES V AND VI.

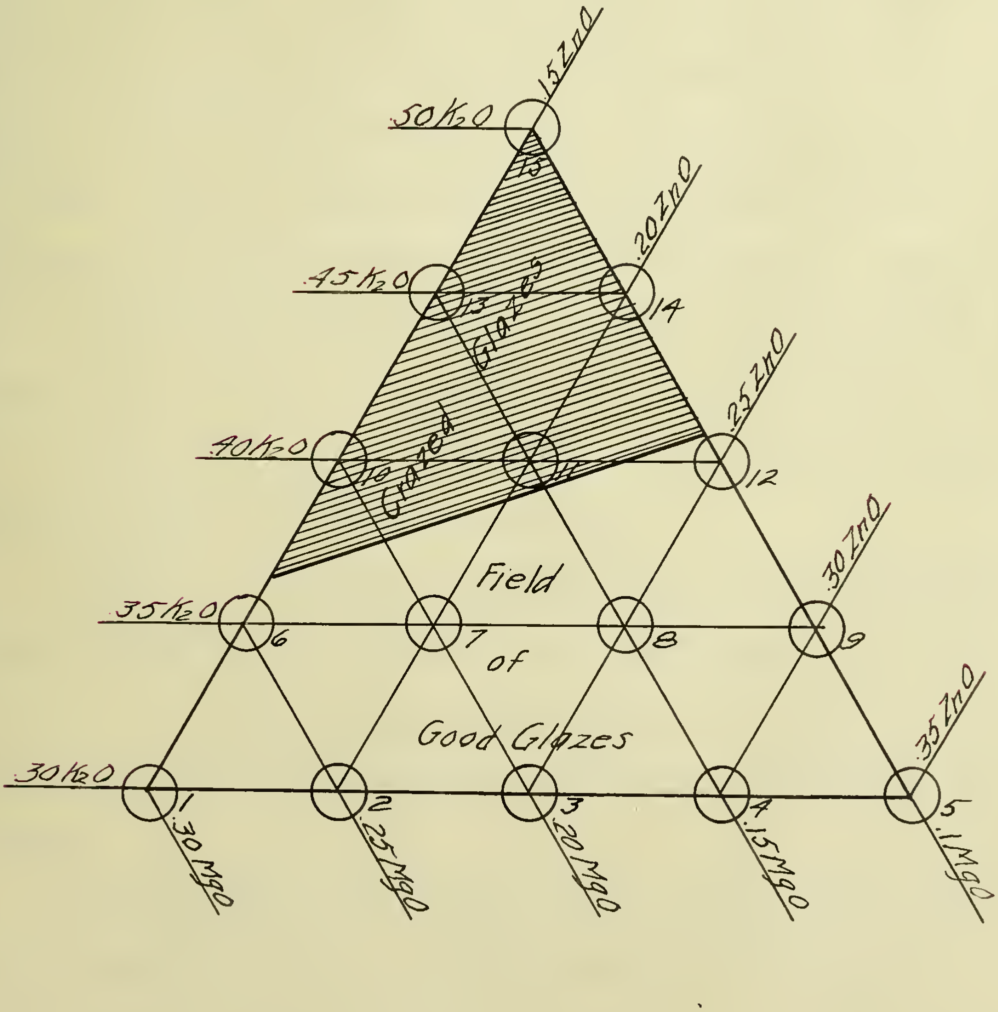
The glazes in this field gave by far the best results

FIGURE III

SERIES V

$$\left.\begin{array}{l} .3\text{-}.5\ K_2O \\ .15\text{-}.35\ ZnO \\ .10\text{-}.30\ MgO \\ .25\ CaO \end{array}\right\} .75\ Al_2O_3\ \ 4.2\ SiO_2$$

Burned to cone 8



obtained at cone 8. Out of the 15 glazes in each series, 10 good glazes were obtained, the other 5 showed crazing evidently due to high spar content. All of the good glazes are opaque, although those which contain only .15 ZnO show the color of the body through. The brilliancy of the surface of these glazes is especially notable, the effect being bright and full of life as contrasted with the dead, dull surface of a high zinc oxide low alumina glaze.

The best glazes in this field are those along the line of .3 K_2O or lowest spar content. The opacity is noticeably decreased by increasing the spar content, and decreasing the clay content. Of the glazes on the line of .3 K_2O those containing .25 ZnO or more are the best, glaze 4 being selected as the best in the entire series, while glazes 3, 8, 12, 9 and 5 are almost as good. Any one of the latter is much whiter and of better texture and brilliancy than the large majority of stone ware glazes now on the market.

Of the two series, Series V with a slightly higher clay content gives more satisfactory results.

Purdy,[1] in Vol. IV., Transactions American Ceramic Society, sets the limit of Al_2O_3 content in a Bristol glaze at .55. In these glazes .75 Al_2O_3 caused absolutely no deleterious effect on the glaze, but exactly the opposite giving good opacity and excellent brilliancy.

In Vol. V of the Transactions,[1] Purdy gives as "the most economical glaze at cone 6 - 7" the following formula:

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1. "Stoneware Glazes" Vol. IV. Transactions American Ceramic Soc.p66
2. "Bristol Glazes" Transactions American Ceramic Society, Vol.V p 165

$$\left.\begin{array}{l} .4\ K_2O \\ .2\ CaO \\ .4\ ZnO \end{array}\right) \ .56\ Al_2O_3\ \ 3.08\ SiO_2$$

Glaze 4 of Series V has the formula

$$\left.\begin{array}{l} .3\ K_2O \\ .25CaO \\ .3\ ZnO \\ .15\ MgO \end{array}\right) \ .75\ Al_2O_3\ \ 4.2\ SiO_2$$

This glaze was weighed up separately to avoid error in blending, dipped and burned to cone 6. It gave a fine white glaze at this temperature. In the original series it had been burned to cone 8, and one trial went to cone 9, so its temperature range is at least cone 6 to 9.

The following table shows the batch weights of the two glazes given above as calculated from the formulae, with an estimate of the cost of materials.

The prices quoted are from the 1909 price list of a representative company, and do not include freight charges, so that the result does not give the actual total cost but shows clearly the comparative costs.

Material	Price	Glaze 4	Series V.	Purdy's	Glaze
	per lb. cents	Weight	Cost	Weight	Cost
Feldspar	.575	38.4	.22	62.9	.36
Clay	.5	26.7	.13	12.2	.06
Flint	.45	20.7	.09	6.4	.03
Whiting	.6	5.7	.03	5.9	.03
Zinc oxide	6.	5.6	.34	9.6	.58
$MgCO_3$	2.	2.9	.06	0	0
Total		100 lbs.	$ .87	100 lbs.	$1.06

The cost of glaze 4 - V is 20% less than the one given by Purdy as his "most successful and economical glaze". He gives his glaze as a cheaper mixture than the stoneware glazes in actual size.

Several glazes in Series V which contain less ZnO than the one selected are very good and would be cheaper than glaze 4, though not so good as to opacity and gloss.

Summary of results on cone 8 series,

(1) A fair degree of opacity may be obtained without the use of zinc oxide or magnesia by increasing the alumina content of the glaze.

(2) A combination of magnesia and zinc gives a better enamel than does zinc alone. This agrees with Stull's results.[1]

(3) To obtain the best results in stoneware glazes at cone 8, the Al_2O_3 content can be as high as .75 equivalents and the spar should not contribute more than .35 equivalents of this. The best proportions of spar being .3 molecular equivalents.

(4) .3 ZnO with about .15 MgO is sufficient to produce a glaze which leaves little to be desired in gloss and whiteness if the rules for low spar and high clay content are observed.

(5) The best total oxygen ratic of acid to base at cone 8 is 1 to 2.5. The best molecular ratio of silica to alumina is 1 to 5.5. The best molecular ratio of ZnO to Al_2O_3 is 1 to 2.5. These also are the ratios given by Purdy.[2]

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1. Stull "A Cheap Enamel for Stoneware". Transactions American Ceramic Society, Vol. X, p. 216.
   Ibid, part II, Vol. XI, p. 613.
2. "Bristol Glazes" Transactions American Ceramic Society, Vol. V, p. 160.

Part II. Enamels at Cones 2 and 3.

The object of this part of the work was to obtain an enamel which might be used as a substitute for the expensive fritted tin-oxide glazes at cone 2.

It was decided to try to "soften down" a good cone 6 Bristol glaze, selected from the previous work, by the use of lead oxide without decreasing the silica and alumina content. (It is quite evident however that the introduction of the lead will sacrifice some of the opacity.)

Series VII and Series VIII were outlined with this end in view.

Series VII and VIII.

Series VII consisted of 15 glazes arranged on a triaxial diagram so that the variation was between ZnO, CaO and PbO.

The corner glazes of the series were

$$\text{Glaze 1}\quad \left.\begin{array}{l} .3\ K_2O \\ .1\ MgO \\ .2\ ZnO \\ .1\ PbO \\ .3\ CaO \end{array}\right)\quad .75\ Al_2O_3 \quad 4.2\ SiO_2$$

$$\text{Glaze 5}\quad \left.\begin{array}{l} .3\ K_2O \\ .1\ MgO \\ .4\ ZnO \\ .1\ PbO \\ .3\ CaO \end{array}\right)\quad .75\ Al_2O_3 \quad 4.2\ SiO_2$$

$$\text{Glaze 15} \quad \left.\begin{array}{l} .3\ K_2O \\ .1\ MgO \\ .2\ ZnO \\ .3\ PbO \\ .1\ CaO \end{array}\right) \quad .75\ Al_2O_3 \quad 4.2\ SiO_2$$

Series VIII had exactly the same limits and variations in the R.O., but the alumina and silica contents were different.

This series was R.O. .67 Al_2O_3 3.75 SiO_2.

These two series were made up and dipped as before, and burned to cone 3 in 21 hours.

Results of Series VII and VIII.

No good glazes were obtained and not much difference in appearance was observed between the extremes of the series. All glazes were white but all of them crawled. Those glazes highest in lead were bubbled as well as crawled.

It was evident from the appearance of these trials that the Al_2O_3 and SiO_2 was much too high for this temperature.

Series IX.

Although it was impossible to select the best combination of oxides from series VII and VIII, it was decided to select an R.O. and vary the silica and alumina content. The R.O. selected was

.3 K_2O

.1 MgO

.1 PbO

.4 ZnO

.1 CaO

Three glazes were made up with this R.O., numbers IX - 1, IX - 16 and IX - 66.

$$\text{Number IX - 1} \quad \left.\begin{array}{l} .3\ K_2O \\ .1\ MgO \\ .1\ PbO \\ .4\ ZnO \\ .1\ CaO \end{array}\right) \quad .70\ Al_2O_3 \quad 3.50\ SiO_2$$

Number IX - 16 - R.O. $.40\ Al_2O_3$ $2.00\ SiO_2$

Number IX - 66 - R.O. $.40\ Al_2O_3$ $2.48\ SiO_2$

The molecular ratios, alumina to silica, of numbers 1 and 16 are the same, 1 to 5.

The oxygen ratios of numbers 1 and 66 are the same, 1 to 2.26.

By blending molecularly numbers 1 and 16, a series was obtained in which the molecular ratio was the same throughout with variable oxygen ratio.

Numbers 1 and 66 when blended, gave a series with constant oxygen ratio and variable molecular ratio of alumina to silica.

Sixteen glazes were blended between the extremes.

Results of Series IX.

Every glaze was white but all had parted or crawled. The crawling was worse at the middle of the series. Those which were highest in silica and alumina "parted" but did not crawl. Those lowest in silica and alumina had parted or cracked and then partly fused over, their texture was dull with a leathery appearance.

No differences were observed due to different molecular or oxygen ratios in the series.

It was evident that the trouble lay in the R.O. and the cause of the crawling was supersaturation with ZnO. .4 ZnO was too high a content at cone 3.

Series X.

A triaxial diagram was constructed varying zinc oxide, magnesia and lead oxide. The lime content was increased to .25 from the .1 molecule in Series IX, and the spar content cut to .25 from .3 molecules.

The series consisted of 21 glazes and the corner glazes were

Glaze 1: .25 K_2O, .25 CaO, .1 ZnO, .3 MgO, .1 PbO) .40 Al_2O_3 2.48 SiO_2

Glaze 6: .25 K_2O, .25 CaO, .3 ZnO, .1 PbO, .1 MgO) .40 Al_2O_3 2.48 SiO_2

Glaze 21: .25 K_2O, .25 CaO, .1 ZnO, .3 PbO, .1 MgO) .40 Al_2O_3 2.48 SiO_2

The silica and alumina was kept lower than was considered necessary as the object was simply to find the best R.O. to work with. The series was burned to cone 3 in 24 hours.

Results of Series X.

All of the glazes "came good" in regards texture and gloss, varying in opacity from No. 21 a practically clear glaze, to No. 6, which with .3 ZnO gave a fair opacity, although the color was gray rather than white. The whitest glaze in the series was No. 1 with .3 MgO, but it also showed the dullest surface of any in the series, being slightly underfired.

The R.O. which gave the best glaze for the purpose in this series was that containing

.25 K_2O

.25 CaO

.26 ZnO

.14 PbO

.10 MgO.

This glaze fitted the body perfectly, was of fair opacity and one of the whitest in the series. It had a fine glossy texture also.

Series XI.

Having established a suitable relation of the oxides it was decided to run a series which should be similar to Series IX in the field covered and amount of variation. The R.O. selected was that of glaze 11, Series X, slightly modified.

$$\text{Glaze 1}\quad \left.\begin{array}{l} .25\ K_2O \\ .25\ CaO \\ .10\ MgO \\ .15\ PbO \end{array}\right)\ .70\ Al_2O_3\ \ 3.50\ SiO_2$$

Glaze 16 - R.O. .40 Al_2O_3 2.00 SiO_2

Glaze 66 - R.O. .40 Al_2O_3 2.48 SiO_2

Glazes blended between 1 and 16 had constant molecular ratio of Al_2O_3 to SiO_2, and variable total oxygen ratio. Those blended between 1 and 66 had the same oxygen ratio with variable molecular ratio.

The series was burned to cone 3 in 28 hours.

Results of Series XI.

The effect of the increase of SiO_2 and Al_2O_3 was to increase the whiteness and opacity of the glaze, but before the best results were obtained in this respect, the glazes began to crawl slightly. Little difference could be observed between the constant molecular ratio and the constant oxygen ratio series.

The best glazes were numbers 10 and 60.

Number 10 - R.O. .52 Al_2O_3 2.6 SiO_2.

Number 60 - R.O. .52 Al_2O_3 2.888 SiO_2

Number 10 is the better of the two being slightly whiter.

Glazes higher in Al_2O_3 and SiO_2 than these, although whiter and working fairly well on the trial pieces, showed a tendency to crawl and would probably not work well commercially.

Glaze number 10 while not as good as a tin enamel is as

white and opaque as the average cone 8 Bristol glaze, and might profitably be used on cheaper wares where a high degree of opacity is not required. There are no ingredients in this glaze which approach the cost of tin oxide and its use would certainly decrease the cost of the glaze batch.

Series XII.

Series XII was an attempt to still further improve the best glazes obtained at this temperature. A triaxial diagram was constructed varying K_2O, MgO and ZnO. Since the spar content was varied the clay content was also varied so that the alumina and silica content was constant.

The limits of the series were

$$1. \quad \left.\begin{array}{l} .15\ K_2O \\ .30\ MgO \\ .15\ ZnO \\ .15\ PbO \\ .25\ CaO \end{array}\right) \ .46\ Al_2O_3 \quad 2.32\ SiO_2$$

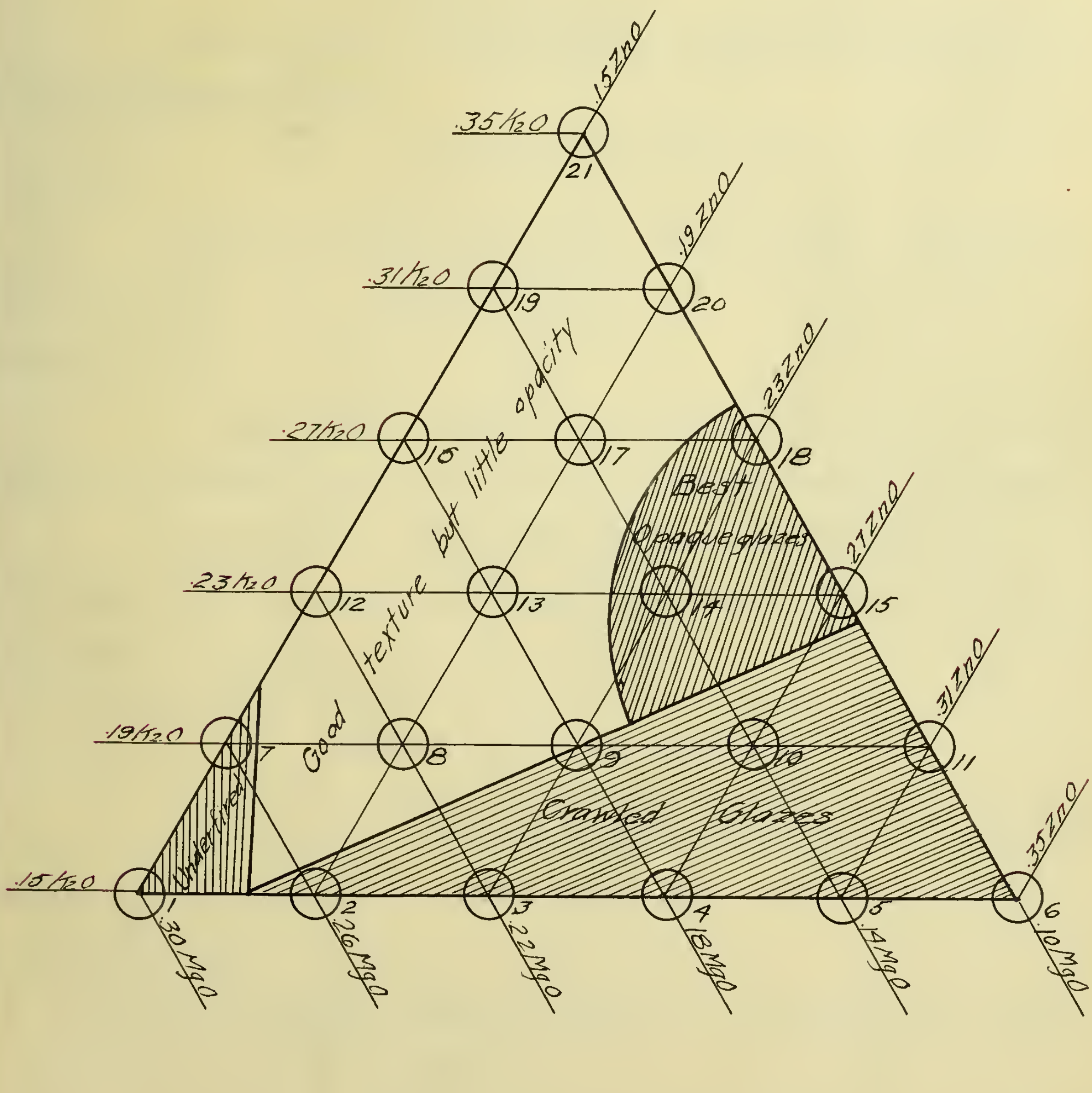
$$6. \quad \left.\begin{array}{l} .15\ K_2O \\ .10\ MgO \\ .35\ ZnO \\ .15\ PbO \\ .25\ CaO \end{array}\right) \ .46\ Al_2O_3 \quad 2.32\ SiO_2$$

FIGURE IV

SERIES XII

$$\left.\begin{array}{l} .15-.35\,K_2O \\ .15-.35\,ZnO \\ .10-.30\,MgO \\ .15\,PbO \\ .25\,CaO \end{array}\right\}\ .46\,Al_2O_3\ 2.32\,SiO_2$$

Burned to cone 3



$$21. \quad \left.\begin{array}{l} .35\ K_2O \\ .10\ MgO \\ .15\ ZnO \\ .15\ PbO \\ .25\ CaO \end{array}\right) \ .46\ Al_2O_3 \quad 2.32\ SiO_2$$

The variation in zinc oxide, potash and magnesia is .4 between adjacent glazes.

Results of Series XII.

Glazes containing high zinc and low spar content were badly crawled. About .25 K_2O, .25 ZnO and .10 MgO gave the best opaque glazes.

No improvement on the best glaze in the last series was obtained although glaze 14 is fairly good as regards whiteness.

The effect of increased spar in cutting down the opacity was evident in this series. Glazes containing above .23 K_2O and less than .2 ZnO were good clear glazes.

Summary on cone 3 Series.

(1) Only a fair degree of whiteness and opacity can be obtained by the use of the same ingredients which produced fine glazes at cone 8.

(2) The best glaze at cone 3 had the following folmula

$$\left.\begin{array}{l} .25\ K_2O \\ .25\ CaO \\ .10\ MgO \\ .15\ PbO \\ .25\ ZnO \end{array}\right) \quad .52\ Al_2O_3 \quad 2.6\ SiO_2$$

This glaze has a total oxygen ratio of 1 to 2.03 and a molecular ratio of Al_2O_3 to SiO_2 of 1 to 5. These gave the best results at cone 3.

(3) In order to obtain good enamels at cone 2 using as small an equivalent of tin oxide as possible, the glaze containing .52 Al_2O_3 would offer a good starting point. The opacity which this glaze already possesses might be intensified by the use of a very small equivalent of tin, and it is highly probable that a fritted glaze would not have to be used.